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Alkoxido, Amido, and Imido Derivatives of Titanium(IV) Tetratolylporphyrin

Abstract

Treatment of (TTP)TiCl₂ (**1**) [TTP = *meso*-5,10,15,20-tetra-*p*-tolylporphyrinato dianion] with excess NaOR (R = Ph, Me, *t*-Bu) affords the bis(alkoxide) derivatives (TTP)Ti(OR)₂ [R = Ph (**2**), Me (**3**), *t*-Bu (**4**)] in moderate yield. The corresponding amido derivative (TTP)Ti(NPh₂)₂ (**5**) is prepared in an analogous fashion employing LiNPh₂. The disubstituted complexes **2**, **3**, and **5** react cleanly with (TTP)TiCl₂ to afford the ligand exchange products (TTP)Ti(OR)Cl [R = Ph (**6**), Me (**7**)] and (TTP)Ti(NPh₂)Cl (**8**), respectively. The monosubstituted complexes **6**–**8** are also obtained by treatment of **1** with 1 equiv of the appropriate NaOR or LiNPh₂ reagent. Treatment of **5** with excess phenol produces the bis(phenoxide) derivative **2** and 2 equiv of HNPh₂. The imido derivatives (TTP)TiNR [R = *t*-Bu (**9**), Ph (**10**), C₆H₄-*p*-Me (**11**)] are prepared by the treatment of **1** with excess LiNHR. The *t*-Bu derivative (**9**) is also obtained by reaction of **1** with excess H₂N-*t*-Bu at elevated temperatures. The phenyl imido complex (**10**) may be produced by the reaction of 0.5 equiv of PhNNPh with (TTP)Ti(η²-EtC≡CEt) in refluxing toluene. Finally, (TTP)TiNTMS (**12**) is obtained by oxidation of (TTP)Ti(η²-EtC≡CEt) with N₃TMS.

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Alkoxido, Amido, and Imido Derivatives of Titanium(IV) Tetratolylporphyrin

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Treatment of (TTP)TiCl₂ (**1**) [TTP = *meso*-5,10,15,20-tetra-*p*-tolylporphyrinato dianion] with excess NaOR (R = Ph, Me, *t*-Bu) affords the bis(alkoxide) derivatives (TTP)Ti(OR)₂ [R = Ph (**2**), Me (**3**), *t*-Bu (**4**)] in moderate yield. The corresponding amido derivative (TTP)Ti(NPh₂)₂ (**5**) is prepared in an analogous fashion employing LiNPh₂. The disubstituted complexes **2**, **3**, and **5** react cleanly with (TTP)TiCl₂ to afford the ligand exchange products (TTP)Ti(OR)Cl [R = Ph (**6**), Me (**7**)] and (TTP)Ti(NPh₂)Cl (**8**), respectively. The monosubstituted complexes **6**–**8** are also obtained by treatment of **1** with 1 equiv of the appropriate NaOR or LiNPh₂ reagent. Treatment of **5** with excess phenol produces the bis(phenoxide) derivative **2** and 2 equiv of HNPh₂. The imido derivatives (TTP)Ti=NR [R = *t*-Bu (**9**), Ph (**10**), C₆H₄-*p*-Me (**11**)] are prepared by the treatment of **1** with excess LiNHR. The *t*-Bu derivative (**9**) is also obtained by reaction of **1** with excess H₂N-*t*-Bu at elevated temperatures. The phenyl imido complex (**10**) may be produced by the reaction of 0.5 equiv of PhN=NPh with (TTP)Ti(η²-EtC≡CEt) in refluxing toluene. Finally, (TTP)Ti=NTMS (**12**) is obtained by oxidation of (TTP)Ti(η²-EtC≡CEt) with N₃TMS.

Introduction

The highly reactive nature of the metal–nitrogen bond in many group 4 imido complexes has lead to a rapidly growing area of research.² For example, group 4 imido complexes can engage in aliphatic and aromatic C–H bond activation processes³ as well as numerous 2 + 2 cycloaddition reactions with unsaturated organic substrates.^{3d} Additionally, group 4 imido complexes have found use in the catalytic hydroamination^{3d} of alkynes and the synthesis of various nitrogen heterocycles.⁴

Recently, we reported the synthesis of a variety of imido–titanium *meso*-tetratolylporphyrinato complexes of the type (TTP)Ti=NR (R = Ph, tolyl, cyclohexyl).⁵ Our interest in these systems stems from our observation that isoelectronic (POR)–Ti=O complexes undergo facile intermetal oxygen atom transfer.⁶ In addition, (POR)Ti=O complexes serve as precatalysts for the epoxidation of alkenes.⁷ In this report, we summarize the preparation and properties of a variety of imido–titanium–porphyrin complexes and discuss their reactivity. Additionally, we report the synthesis and reactivity of new alkoxide and amide derivatives of titanium–porphyrin. These new complexes extend the class of group 4 porphyrin complexes possessing hard π-donor ligands.⁸

Experimental Section

General. All manipulations were performed under an inert atmosphere of nitrogen using a Vacuum Atmospheres glovebox equipped with a Model MO40-1 Dri-Train gas purifier. The glovebox atmosphere was continuously monitored with an Illinois Instrument Model 2550 trace oxygen analyzer. The concentration of O₂ in the glovebox was kept at less than 5 ppm at all times. All solvents were rigorously degassed and dried prior to use. Benzene-*d*₆, toluene, and hexane were freshly distilled from purple solutions of sodium benzophenone and brought into the drybox without exposure to air. (TTP)TiCl₂ (**1**) was prepared according to published procedures⁹ and recrystallized from CH₂Cl₂/hexane prior to use. Phenol was purchased from Aldrich and used as received. Methanol was purchased from Fisher, dried with CaH₂, and vacuum transferred prior to use. NaOR (R = Ph, Me, *t*-Bu) reagents were prepared by treating the appropriate alcohol with sodium in hexanes. Diphenylamine was purchased from Fisher and was recrystallized from hexanes prior to use. LiNPh₂ was prepared by reaction of the free amine with *n*-butyllithium in hexanes. The lithium amide salts, LiNHPh, LiNHC₆H₄-*p*-Me, and LiNHC₆H₁₁ were prepared as previously described.⁵ LiNH-*t*-Bu was prepared by the reaction of H₂N-*t*-Bu with *n*-butyllithium in hexanes and was recrystallized from hexanes at –20 °C. All amines used above were purchased from Aldrich and were purified by literature methods.¹⁰ N₃TMS was purchased from Aldrich and used as received.

¹H NMR data were recorded at 20.0 °C on either a Varian VXR (300 MHz) or a Bruker DXR (400 MHz) spectrometer. Chemical shifts are referenced to proton solvent impurities (δ 7.15, C₆D₅H). UV–vis data were recorded on a HP8452A diode array spectrophotometer. Elemental analyses (C, H, N) were performed by Atlantic Microlab of Norcross, Georgia. All samples were handled under nitrogen and WO₃ was used as a combustion aid. MS–CI studies were performed on a Finnigan TSQ 700 at 70 eV in the negative ion mode using ammonia as the ionization gas.

(TTP)Ti(OPh)₂ (**2**). (TTP)TiCl₂ (200 mg, 0.254 mmol) and NaOPh (62 mg, 0.53 mmol) were stirred in toluene (ca. 10 mL) to afford a

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- (1) Presidential Young Investigator (1990–1995) and Camille and Henry Dreyfus Teacher-Scholar (1993–1998).
- (2) For a comprehensive review of transition metal imido complexes, see: Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.
- (3) For examples in Ti chemistry, see: (a) Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. J. *Am. Chem. Soc.* **1991**, *113*, 2985. (b) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179. For examples in Zr chemistry, see: (c) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (d) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708. (e) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705. (f) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.
- (4) (a) McGrane, P. L.; Livinghouse, T. *J. Org. Chem.* **1992**, *57*, 1323. (b) McGrane, P. L.; Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1992**, *114*, 5459. (c) McGrane, P. L.; Livinghouse, T. *J. Am. Chem. Soc.* **1993**, *115*, 11485.
- (5) Berreau, L. M.; Young, V. G., Jr.; Woo, L. K. *Inorg. Chem.* **1995**, *34*, 527–529.
- (6) Woo, L. K.; Hayes, J. A.; Goll, J. G. *J. Inorg. Chem.* **1990**, *29*, 3916.
- (7) Ledon, H. J.; Varscan, F. *Inorg. Chem.* **1984**, *23*, 2735.

- (8) For examples of Zr–porphyrin complexes with hard π-donors, see: (a) Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 2266. (b) Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655. For a review of recent advances in early transition metal porphyrin chemistry, see: Brand, H.; Arnold, J. *Coord. Chem. Rev.* **1995**, *140*, 137 and references therein.
- (9) Berreau, L. M.; Hays, J. A.; Young, V. G., Jr.; Woo, L. K. *Inorg. Chem.* **1994**, *33*, 105–108.
- (10) Perrin, D. D.; Armagego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.

light brown solution which became an opaque deep brown color after several minutes. After 4 h, the solution was filtered. Removal of solvent from the filtrate under reduced pressure afforded (TTP)Ti(OPh)₂ (123 mg, 0.137 mmol, 54% yield) as a semicrystalline, analytically pure, deep blue solid. UV-vis (toluene): 330, 338, 382, 424 (Soret), 484, 488, 608, 654 nm. ¹H NMR (C₆D₆, 300 MHz): 9.02 (s, 8H, β-H), 8.01 (d, 8H, ³J_{H-H} = 7.8 Hz, -C₆H₄Me), 7.26 (d, 8H, ³J_{H-H} = 7.8 Hz, -C₆H₄Me), 2.38 (s, 12H, -C₆H₄Me), 5.83 (overlapping d and t, 6H, *m-p*-C₆H₅), 2.67 (m, 2H, *o*-C₆H₅). Anal. Calcd for C₆₀H₄₅N₄O₂Ti: C, 79.81; H, 5.13; N, 6.20. Found: C, 80.58; H, 5.44; N, 6.06.

(TTP)Ti(OMe)₂ (3). (TTP)TiCl₂ (158 mg, 0.20 mmol) and NaOMe (122, 2.25 mmol) were slurried in toluene and the resultant brown solution was rapidly stirred. After 5 h, the solution was filtered and the solvent was removed from the dark brown filtrate to afford blue (TTP)Ti(OMe)₂ (100 mg, 0.129 mmol, 66% yield). Despite numerous efforts to obtain analytically pure compound, **3** consistently contains a trace (ca. 5%) of (TTP)Ti=O impurity which precluded elemental analysis. UV-vis (toluene): 426 (Soret), 552 nm. ¹H NMR (C₆D₆, 300 MHz): 9.07 (s, 8H, β-H), 8.07 (d, 8H, ³J_{H-H} = 7.8 Hz, -C₆H₄Me), 7.26 (d, 8H, ³J_{H-H} = 7.8 Hz, -C₆H₄Me), 2.39 (s, 12H, -C₆H₄Me), -0.83 (s, 6H, OCH₃). MS (CI) Calcd (found) *m/e*: [M⁺] 778 (778).

(TTP)Ti(O-*t*-Bu)₂ (4). (TTP)TiCl₂ (44 mg, 0.056 mmol) and NaO-*t*-Bu (26 mg, 0.28 mmol) were slurried in toluene and the resultant brown solution was rapidly stirred at ambient temperature. After 5 h, the solution was filtered and the solvent was removed from the dark brown filtrate to afford blue (TTP)Ti(O-*t*-Bu)₂ (32 mg, 0.037 mmol, 67% yield). Despite numerous efforts to obtain an analytically pure compound, **4** consistently contained traces (ca. 5%) of impurities which precluded elemental analysis. UV-vis (toluene): 450 (Soret), 584, 622 nm. ¹H NMR (C₆D₆, 300 MHz): 9.05 (s, 8H, β-H), 8.23 (d, 8H, ³J_{H-H} = 7.8 Hz, -C₆H₄Me), 7.31 (d, 8H, ³J_{H-H} = 7.8 Hz, -C₆H₄Me), 2.40 (s, 12H, -C₆H₄Me), -2.18 (s, 18H, O-*t*-Bu).

(TTP)Ti(NPh₂)₂ (5). (TTP)TiCl₂ (326 mg, 0.413 mmol) and LiNPh₂ (150 mg, 0.0859 mmol) were slurried in hexanes (ca. 20 mL). The solution slowly changed from light brown to chocolate brown. After 5 h, the solution was filtered to collect a dark brown solid. This solid was placed on a clean fritted filter and extracted with CH₂Cl₂ (3 × 3 mL). Removal of solvent from the resultant filtrate afforded (TTP)Ti(NPh₂)₂ (251 mg, 0.238 mmol, 58% yield) as a semicrystalline, blue solid. UV-vis (toluene): 426 (Soret), 552 nm. ¹H NMR (C₆D₆, 400 MHz): 8.83 (s, 8H, β-H), 8.09 (d, 8H, ³J_{H-H} = 7.6 Hz, -C₆H₄Me), 7.37 (d, 8H, ³J_{H-H} = 7.6 Hz, -C₆H₄Me), 6.17 (d, 2H, ³J_{H-H} = 7.2 Hz, C₆H₅), 6.05 (d, 4H, ³J_{H-H} = 7.2 Hz, C₆H₅), 2.86 (d, 4H, ³J_{H-H} = 7.2 Hz, C₆H₅), 2.44 (s, 12H, -C₆H₄Me). Anal. Calcd for C₇₂H₅₆N₆Ti: C, 82.11; H, 5.36; N, 7.98. Found: C, 81.58; H, 5.98; N, 7.56.

(TTP)Ti(OPh)Cl (6). (TTP)TiCl₂ (45 mg, 0.058 mmol) and LiOPh (6 mg, 0.06 mmol) were stirred in toluene (ca. 10 mL). The initial dark brown color of the solution progressively darkens to a nearly black color. After 15 h, the solution was filtered and solids on the frit were extracted with toluene. The solvent was removed from the combined filtrates under reduced pressure to yield (TTP)Ti(OPh)Cl (31 mg, 0.37 mmol, 64% yield) as a deep blue solid. UV-vis (toluene): 352, 404, 426 (Soret), 552 nm. ¹H NMR (C₆D₆, 400 MHz): 9.04 (s, 8H, β-H), 7.94 (d, 8H, ³J_{H-H} = 7.6 Hz, -C₆H₄Me), 7.24 (m, 8H, -C₆H₄Me), 5.77 (t, 1H, ³J_{H-H} = 7.2 Hz, -OC₆H₅), 5.69 (t, 2H, ³J_{H-H} = 7.2 Hz, -OC₆H₅), 2.72 (d, 2H, ³J_{H-H} = 8.0 Hz, -OC₆H₅), 2.37 (s, 12H, -C₆H₄Me). MS (CI) Calcd (found) *m/e*: [(TTP)TiOPh]⁺ 767 (767); [(TTP)TiCl]⁺ 751 (751).

(TTP)Ti(OMe)Cl (7). (TTP)TiCl₂ (56 mg, 0.72 mmol) and LiOMe (3 mg, 0.08 mmol) were dissolved in toluene (ca. 10 mL) to give a deep brown solution. After 4 h, the nearly black solution was filtered. The solid left on the frit was extracted with toluene and CH₂Cl₂. Removal of the solvent from the resultant filtrate under reduced pressure afforded (TTP)Ti(OMe)Cl (20 mg, 36% yield) as a deep blue, microcrystalline solid which is slightly contaminated with (TTP)TiCl₂ (ca. 5%), presumably due to stoichiometry deficiencies. UV-vis (toluene): 376, 426 (Soret), 502 nm. ¹H NMR (C₆D₆, 300 MHz): 9.08 (s, 8H, β-H), 8.07 (d, 4H, ³J_{H-H} = 7.8, -C₆H₄Me), 7.90 (d, 4H, ³J_{H-H} = 7.8, -C₆H₄Me), 7.26 (d, 4H, ³J_{H-H} = 8.1, -C₆H₄Me), 7.21 (d, 4H, ³J_{H-H} = 8.1, -C₆H₄Me), 2.38 (s, 12H, -C₆H₄Me), -0.79 (s, 3H, -OMe). MS(CI) Calcd (found) *m/e*: [(TTP)TiClO]⁺, 767 (767); [(TTP)TiCl]⁺, 751 (751).

Reaction of (TTP)TiCl₂ with *t*-BuOH. An anaerobic C₆D₆ (0.7 mL) solution of (TTP)TiCl₂ (20 mg, 0.026 mmol) and *t*-BuOH (14 μL, 0.15 mmol) was sealed in an NMR tube under N₂. The mixture was monitored by ¹H NMR until no further reaction was observed. The only new species observed in solution were (TTP)Ti(O-*t*-Bu)Cl (80%) and (TTP)Ti=O (7%). Unreacted (TTP)TiCl₂ (13%) and *t*-BuOH were also present. ¹H NMR signals for (TTP)Ti(O-*t*-Bu)Cl (300 MHz): 9.06 (s, 8H), 8.13 (d, 4H, ³J_{H-H} = 7.8 Hz, -C₆H₄Me), 7.92 (d, 4H, ³J_{H-H} = 7.8 Hz, -C₆H₄Me), 7.29 (m, 8H, -C₆H₄Me), 2.38 (s, 12H, -C₆H₄Me), -2.25 (s, 9H, *t*-Bu).

(TTP)Ti(NPh₂)Cl (8). In a general procedure, approximately 1 equiv of LiNPh₂ was added to (TTP)TiCl₂. For example, (TTP)TiCl₂ (53 mg, 0.067 mmol) and LiNPh₂ (13 mg, 0.073 mmol) were stirred in hexanes (ca. 10 mL). The initial light brown solution gradually darkened to deep brown solution. After 4 h, the solution was filtered and the solvent was removed from the filtrate under reduced pressure to afford (TTP)Ti(NPh₂)Cl (27 mg, 0.029 mmol, 43% yield) as a deep blue solid. Due to minor differences in stoichiometry, compound **8** is consistently contaminated with (TTP)TiCl₂ or (TTP)Ti(NPh₂)₂ (ca. 5%). Even with several recrystallizations, these impurities could not be removed and hence preclude elemental analysis. UV-vis (toluene): 372, 428 (Soret), 554 nm. ¹H NMR (C₆D₆, 300 MHz): 8.98 (s, 8H, β-H), 8.05 (d, 4H, ³J_{H-H} = 7.8, -C₆H₄Me), 7.88 (d, 4H, ³J_{H-H} = 7.8, -C₆H₄Me), 7.44 (m, 8H, -C₆H₄Me), 2.41 (s, 12H, -C₆H₄Me), 6.12 (t, 2H, ³J_{H-H} = 7.2, *p*-H), 5.96 (t, 4H, ³J_{H-H} = 7.2, *m*-H), 2.83 (d, 4H, ³J_{H-H} = 7.2, *o*-H). MS (CI) Calcd (found) *m/e*: [(TTP)TiCl]⁺, 751 (751); [(TTP)Ti(NPh₂)Cl-H]⁺, 918 (918).

(TTP)Ti=N-*t*-Bu (9). (TTP)TiCl₂ (101 mg, 0.13 mmol) and LiNH-*t*-Bu (21 mg, 0.27 mmol) were dissolved in toluene (ca. 10 mL) to afford a deep red solution. After 5 min, the solution was filtered and the resultant deep red filtrate was taken to dryness under reduced pressure to afford (TTP)Ti=N-*t*-Bu (95 mg, 0.12 mmol, 94% yield) as a semicrystalline, purple solid. Analytically pure samples could be obtained by recrystallization from toluene/hexane solution at -20 °C. UV-vis (toluene): 424 (Soret), 548 nm. ¹H NMR (C₆D₆, 300 MHz): 9.24 (s, 8H, β-H), 8.32 (d, ³J_{H-H} = 7.65 Hz, 4H, -C₆H₄Me), 8.04 (d, ³J_{H-H} = 7.05 Hz, 4H, -C₆H₄Me), 7.34 (d, *J* = 5.70 Hz, -C₆H₄Me), 7.30 (d, *J* = 5.70 Hz, -C₆H₄Me), 2.42 (s, 12H, -C₆H₄-CH₃), -1.58 (s, 9H, *t*-Bu). Anal. Calcd for C₅₂H₄₅N₅Ti: C, 79.28; H, 5.76; N, 8.89. Found: C, 79.34; H, 5.76; N, 8.75.

(TTP)Ti=NPh (10). (TTP)TiCl₂ (104 mg, 0.132 mmol) and LiNPh (50 mg, 0.51 mmol) were dissolved in toluene (ca. 15 mL). The solution gradually turned a deep red color. After 30 min, the solution was filtered to remove a black solid and the resultant ruby filtrate was taken to dryness under reduced pressure. This afforded (TTP)Ti=NPh (94 mg, 0.12 mmol, 88% yield) as a purple solid. Analytically pure samples could be obtained by recrystallization from toluene/hexanes at -20 °C. UV-vis (toluene): 426 (Soret), 548 nm. ¹H NMR (C₆D₆, 300 MHz): 9.21 (s, 8H, β-H), 8.14 (d, 4H, -C₆H₄-CH₃), 8.03 (d, 4H, -C₆H₄-CH₃), 7.30 (d, 8H, -C₆H₄-CH₃), 5.72 (m, 3H, *m*, *p*-H), 3.85 (d, 2H, *o*-H), 2.41 (s, 12H, -C₆H₄-CH₃). MS(EI) Calcd (found) (*m/e*): 806 (807), [M]⁺. Anal. Calcd for C₅₄H₄₁N₅Ti: C, 80.29; H, 5.12; N, 8.67. Found: C, 79.26; H, 5.48; N, 8.28.

(TTP)Ti=NC₆H₄-*p*-Me (11). (TTP)TiCl₂ (82 mg, 0.104 mmol) and LiNHC₆H₄Me (45 mg, 0.40 mmol) were dissolved in toluene (ca. 15 mL) to produce a red solution. After 4 h, the solution was filtered and the resultant deep red filtrate was taken to dryness under reduced pressure to afford (TTP)Ti=NC₆H₄-*p*-Me (74 mg, 0.09 mmol, 87% yield) as a purple-red solid. Analytically pure samples could be obtained by recrystallization from toluene/hexanes at -20 °C. UV-vis (toluene): 426 (Soret), 548 nm. ¹H NMR (C₆D₆, 300 MHz): 9.21 (s, 8H, β-H), 8.15 (d, 4H, -C₆H₄-CH₃), 8.04 (d, 4H, -C₆H₄-CH₃), 7.30 (d, 8H, -C₆H₄-CH₃), 5.53 (d, 2H, *m*-H), 3.81 (d, 2H, *o*-H), 2.41 (s, 12H, -C₆H₄-CH₃), 1.29 (s, 3H, -CH₃). Anal. Calcd for C₅₅H₄₃N₅Ti: C, 80.36; H, 5.28; N, 8.52. Found: C, 80.29; H, 5.47; N, 8.20.

(TTP)Ti=NTMS (12). (TTP)Ti(η²-EtC≡CEt) (105 mg, 0.132 mmol) was dissolved in toluene (ca. 10 mL), and neat N₃TMS (ca. 0.5 mL, ca. 4.0 mmol) was added to the rapidly stirred solution. Evolution of gas was observed, and after 16 h, the solution was taken to dryness under reduced pressure to afford a dark oil. The oil was dissolved in a minimum of toluene (ca. 2 mL), and the solution was layered with hexanes (ca. 6 mL). After cooling the solution at -20 °C for 14 h,

deep purple crystals formed. The crystals were collected by filtration and dried in vacuo to afford analytically pure (TTP)Ti=NTMS (40 mg, 0.050 mmol, 38% yield). UV-vis (toluene): 428 (Soret), 550 nm. ^1H NMR (C_6D_6 , 300 MHz): 9.25 (s, 8H, $\beta\text{-H}$), 8.31 (d, $^3J_{\text{H-H}} = 9.0$ Hz, 4H, $-\text{C}_6\text{H}_4\text{Me}$), 8.00 (d, $^3J_{\text{H-H}} = 9.0$ Hz, 4H, $-\text{C}_6\text{H}_4\text{Me}$), 7.32 (m, 8H, $-\text{C}_6\text{H}_4\text{Me}$), 2.42 (s, 12H, $-\text{C}_6\text{H}_4-\text{CH}_3$), -2.04 (s, 9H, SiCH_3). Anal. Calcd for: $\text{C}_{51}\text{H}_{45}\text{N}_5\text{SiTi}$: C, 76.20; H, 5.64; N, 8.71. Found: C, 76.04; H, 5.99; N, 8.04.

Results

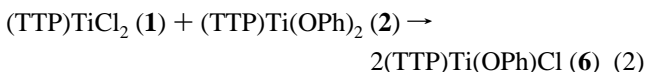
Synthesis and Properties of Bis(alkoxide) Complexes. The titanium(IV) tetratolylporphyrinato complex (TTP)TiCl₂ (**1**) reacts readily with sodium phenoxide in toluene to afford the blue, bis(phenoxide) complex (TTP)Ti(OPh)₂ (**2**) in moderate yield (eq 1). The bis(alkoxide) complexes (TTP)Ti(OMe)₂ (**3**)



and (TTP)Ti(O-*t*-Bu)₂ (**4**) are obtained in an analogous fashion. Complexes **2** and **3** have also been prepared by the reaction of **1** with 2 equiv of the free alcohols in the presence of piperidine, which serves to scavenge the HCl byproduct. The ^1H NMR spectra of these complexes are consistent with the alkoxide ligands being arranged in a trans geometry. In particular, the H_o and H_m protons of the tolyl groups of the [TTP]²⁻ ligand appear as two sharp sets of doublets. These data indicate that the molecule possesses a mirror plane through the center of the porphyrin and an approximate D_{4h} symmetry. In the ambient temperature ^1H NMR spectrum of **2** in C_6D_6 , the protons of the phenoxide ligands appear at 2.67 ppm (H_o) and 5.83 ppm (H_m and H_p). The large upfield shift of these protons is representative of ligands above the porphyrin plane. Similarly, a strong upfield shift is observed for the Me groups of the methoxide ligands in **3**.

In the solid state, complex **2** is inert and remains unchanged for more than 4 months in air. The bis(phenoxide) is also stable to hydrolysis in solution with excess water for more than 1 week. In contrast, exposure of a solution of the bis(methoxide) to air results in instantaneous and quantitative conversion to the oxo complex (TTP)Ti=O. Treatment of (TTP)Ti(OR)₂ (R = Me, *t*-Bu) with excess phenol cleanly produces (TTP)Ti(OPh)₂ and ROH. In general, the spontaneous reaction involves the most basic ligand becoming protonated. Thus, treatment of (TTP)Ti(OPh)₂ with 7.6 equiv MeOH produces only 0.3 equiv of (TTP)Ti(OPh)(OMe) and 0.1 equiv of (TTP)Ti(OMe)₂.

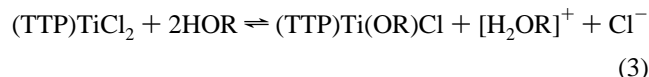
In solution **2** has been found to engage readily in intermetal ligand exchange reactions. Thus, treatment of **2** with 1 equiv of (TTP)TiCl₂ in toluene rapidly (ca. 10 min) and quantitatively affords a new product, **6**, in high yield. The ^1H NMR spectrum of **6** displays an aa'mm' pattern for the porphyrin tolyl protons. Thus, the porphyrin plane does not serve as a mirror plane of symmetry in this new molecule. In addition, the porphyrin tolyl ligands are not freely rotating about the $\text{C}_{\text{meso}}-\text{C}_{\text{ipso}}$ bond on the NMR timescale. Accordingly, this new complex is formulated as (TTP)Ti(OPh)Cl (**6**) (eq 2). Complex **6** is also prepared



by the reaction of (TTP)TiCl₂ with 1 equiv of NaOPh in toluene. The monomethoxide complex, (TTP)Ti(OMe)Cl has also been synthesized by both of these routes. Interestingly, the intermetal ligand redistribution reaction described in eq 2, unlike previously reported exchanges for (TTP)Ti(IV) complexes, appears to be

driven to completion. The reverse process, disproportionation of (TTP)Ti(OPh)Cl (**6**) to (TTP)TiCl₂ and (TTP)Ti(OPh)₂, has not been observed by either variable temperature ^1H NMR experiments or UV-vis studies.

Alcohols are not sufficiently basic to displace both chloro ligands in (TTP)TiCl₂. Instead an equilibrium is established for monoalkoxide formation as represented in eq 3. In a mixture



of 2.7 PhOH and (TTP)TiCl₂ in C_6D_6 , the equilibrium lies far to the left. No monophenoxide complex is detected by ^1H NMR. When 6.7 equiv of MeOH is added to (TTP)TiCl₂ in C_6D_6 , the equilibrium ratio of (TTP)Ti(OMe)Cl to (TTP)TiCl₂ is 0.37:1. With the more basic *tert*-butanol (5.8 equiv), the resulting ratio of (TTP)Ti(O-*t*-Bu)Cl to (TTP)TiCl₂ is 6.2:1. Addition of an exogenous base drives the reaction completely to bis(alkoxide) formation. Thus, injection of 3 equiv of piperidine into an equilibrated NMR tube containing (TTP)TiCl₂ and *tert*-butanol in C_6D_6 resulted in quantitative formation of (TTP)Ti(O-*t*-Bu)₂.

Preparation of Bis(amido) Complexes. Treatment of freshly prepared (TTP)TiCl₂ with ≥ 2 equiv of LiNPh₂ in hexanes results in the formation of the bis(amido) complex (TTP)Ti(NPh₂)₂ (**5**) in modest yield (eq 4). This reaction is



very sensitive to solvent choice. In our hands, **5** could not be produced in pure fashion employing toluene, benzene, THF, or CH_2Cl_2 as a solvent. In these solvents, intractable paramagnetic (presumably Ti(III)) species are formed. Another difficulty in preparing **5** is its extreme moisture-sensitivity. Complex **5** decomposes instantaneously in air to afford (TTP)Ti=O and free HNPh₂. Our attempts to prepare other bis(amido) complexes have met with no success. Thus, the reaction of **1** with LiNEt₂, LiNTMS₂, LiN(C₆H₁₁)₂, TMSNEt₂, or lithium tetrahydroquinolide, under similar conditions employed to produce **5**, leads only to intractable, paramagnetic products. Finally, treatment of **5** with other secondary amines, such as HNEt₂, piperidine, *t*-BuNH₂, or 1,2,3,4-tetrahydroquinoline, did not result in the production of any new bis(amido) transamination products. These observations parallel those described for the alkoxide/alcohol system. The equilibrium favors the complex bound to the least basic secondary amide.

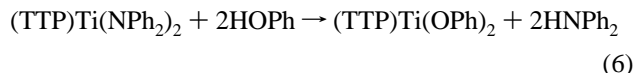
Analogous to the bis(alkoxide) complexes discussed above, the diphenylamido ligands in **5** are disposed in a trans fashion. Thus, **5** displays pseudo D_{4h} symmetry in the ambient temperature ^1H NMR spectrum. In C_6D_6 , the resonances for phenyl groups of the NPh₂ ligands are shifted upfield [δ 6.17 (H_p), δ 6.05 (H_m), and δ 2.86 (H_o)] relative to the free amine, again due to their proximity to the porphyrin ring current.

Like the bis(alkoxide) derivatives, the bis(amido) complex undergoes rapid ligand redistribution upon treatment with 1 equiv of (TTP)TiCl₂ to afford the monoamido complex (TTP)Ti(NPh₂)Cl (**8**) (eq 5). Again, this reaction appears to be entirely irreversible. Complex **8** can be prepared independently from treatment of **1** with 1 equiv of LiNPh₂.

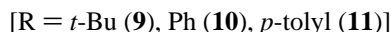
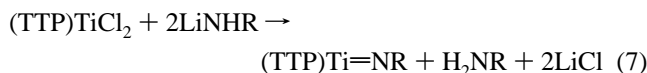


As is typical for early transition metal amido complexes, **5** undergoes rapid alcoholysis with phenol to afford (TTP)Ti(OPh)₂ (**2**) (eq 6). Not surprisingly, this reaction is irreversible.

Complex **2** does not react with HNPh₂ to any observable extent. This behavior is attributed to the acidity of phenol relative to diphenylamine. Correspondingly, water rapidly converts (TTP)-Ti(NPh₂)₂ to the oxo complex, (TTP)Ti=O.

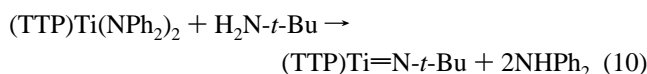
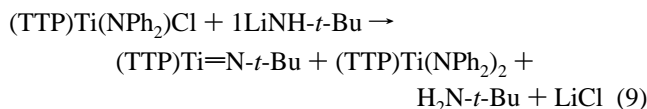
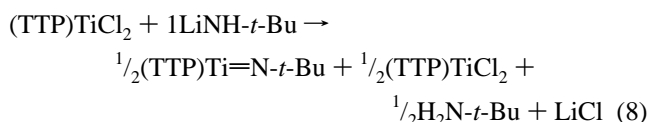


Preparation of Imido Complexes. From Ti(IV) Species via α -Hydrogen Abstraction. Treatment of (TTP)TiCl₂ with 2 equiv of LiNH-*t*-Bu in toluene results in the formation of the imido derivative (TTP)Ti=N-*t*-Bu (**9**) (eq 7). This reaction is



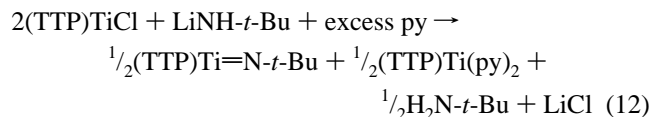
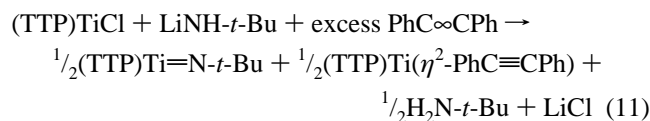
extremely clean and proceeds quantitatively in C₆D₆ to afford **9** along with 1 equiv of *tert*-butylamine (¹H NMR, Ph₃CH internal standard). The ¹H NMR spectrum (C₆D₆) of **9** reveals four doublets assignable to the H_o, H_{o'}, H_m, and H_{m'} resonances of the [TTP]²⁻ ligand, indicating the expected lack of a mirror plane of symmetry coincidental with the porphyrin plane. The protons of the *t*-Bu group are shifted strongly upfield (δ -1.54 ppm), which as discussed above, is diagnostic for axially bound ligands in porphyrin systems. Analogous preparations have been employed to synthesize the series (TTP)Ti=NR [R = Ph (**10**), *p*-tolyl (**11**)] all of which are obtained in high yield (eq 7). Attempts to prepare the parent imido complex by treatment of **1** with LiNH₂ have, thus far, proved unsuccessful.

As noted above, with the secondary lithium amide, LiNPh₂, we can prepare the monosubstituted amido complex (TTP)Ti(NPh₂)Cl. However, with primary lithium amides this is not possible. For example, treatment of **1** with 1 equiv of LiNH-*t*-Bu failed to produce any (TTP)Ti(NH-*t*-Bu)Cl. Instead, this reaction led to the formation of a half equivalent of (TTP)Ti=N-*t*-Bu (**9**) and left an equimolar amount of unreacted **1** (eq 8). The reaction of (TTP)Ti(NPh₂)Cl, a model complex for (TTP)-Ti(NHR)Cl, with 1 equiv of LiNH-*t*-Bu *did not* allow the isolation or observation of the mixed amido complex (TTP)-Ti(NPh₂)(NH-*t*-Bu). Instead, the only spectroscopically observable products at early times (\sim 10 min) were (TTP)Ti=N-*t*-Bu, the bis(amido) complex (TTP)Ti(NPh₂)₂, formed in an approximate 1:1 ratio along with free H₂N-*t*-Bu (eq 9). The bis(amido) complex apparently forms from displaced NPh₂, which undergoes metathesis with unreacted (TTP)Ti(NPh₂)Cl. After long reaction times (>10 h), the final products were (TTP)-Ti=N-*t*-Bu and free HNPh₂ from the subsequent reaction between (TTP)Ti(NPh₂)₂ and H₂N-*t*-Bu. This latter process was confirmed independently. Treatment of (TTP)Ti(NPh₂)₂ with excess H₂N-*t*-Bu quantitatively produced (TTP)Ti=N-*t*-Bu and HNPh₂ (eq 10).

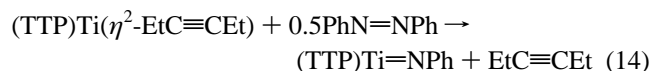
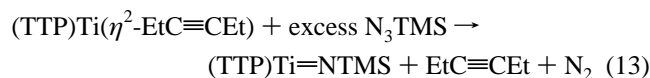


It has been previously reported that treatment of (TTP)TiCl₂ with excess aniline *does not* produce the imido derivative, (TTP)Ti=NPh (**10**).¹¹ In accord with this earlier report, we have confirmed that the arylimido complexes cannot be synthesized in this manner. Thus, under similar conditions, **1** is unreactive toward *p*-toluidine. We have found, however, that heating toluene solutions of **1** with excess *tert*-butylamine produces (TTP)Ti=N-*t*-Bu (**9**) in high yield along with [H₃N-*t*-Bu]Cl byproduct.

Imido Complexes Via Disproportionation of Ti(III). We have also found that Ti(IV)-imido complexes can be produced from Ti(III)-precursor complexes. For example, toluene solutions of (TTP)TiCl react instantaneously with LiNH-*t*-Bu in the presence of PhC \equiv CPh to provide (TTP)Ti=N-*t*-Bu (**9**) and the known alkyne adduct, (TTP)Ti(η^2 -PhC \equiv CPh)^{12a} in a 1:1 ratio (eq 11). Similarly, reaction of (TTP)TiCl with 1 equiv of LiNH-*t*-Bu followed by the addition of excess pyridine affords 0.5 equiv of the imido complex **9** along with 0.5 equiv of (TTP)-Ti(py)₂ (eq 12). These disproportionation reactions underscore the strong thermodynamic driving force for the formation of these robust Ti(IV)-imido complexes.



Imido Complexes via Oxidation of Ti(II) Complexes. Imido complexes are available from the oxidation of Ti(II) complexes with [NR]²⁻ sources. For example, the Ti(II) alkyne complex (TTP)Ti(η^2 -EtC \equiv CEt) reacts instantaneously with excess N₃TMS in toluene to provide the imido complex (TTP)-Ti=NTMS (**12**) and 1 equiv of free EtC \equiv CEt (eq 13). Additionally, treatment of (TTP)Ti(η^2 -EtC \equiv CEt) with 0.5 equiv PhN=NPh in refluxing toluene provides (TTP)Ti=NPh (**10**) as the sole porphyrin product (eq 14).¹³ Details of this reaction will be reported elsewhere.¹⁴



Reactivity of Ti-Imido Complexes. The imido complexes described above show only limited reactivity. As expected, treatment of (TTP)Ti=NR complexes with alcohols such as phenol and methanol results in the clean formation the bis-(alkoxide) complexes **2** and **3**, respectively along with free amine. Unlike previously reported Ti-imido complexes,¹⁵

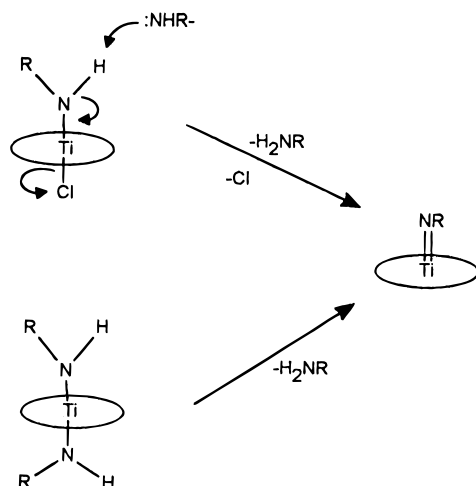
(11) Buchler, J. W.; Pfeifer, S. Z. *Naturforsch., B: Chem. Sci.* **1985**, *40B*, 1362.

(12) (a) Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102. (b) Woo, L. K.; Hays, J. A.; Young, V. G., Jr.; Day, C. L.; Caron, C.; D'Souza, F.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4186.

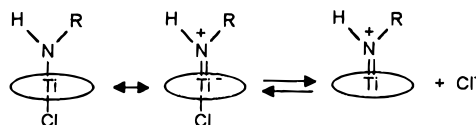
(13) For other examples of azobenzene cleavage leading to imido complexes in Ti chemistry, see: (a) Hill, J. E.; Profflet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664. (b) Duchateau, R.; Williams, A. J.; Gambarotta, S.; Chiang, M. Y. *Inorg. Chem.* **1991**, *30*, 4863.

(14) Gray, S. D.; Woo, L. K. Unpublished results.

Scheme 1



Scheme 2

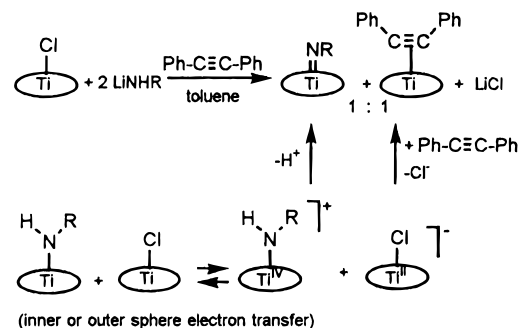


(TTP)Ti=NR complexes do not undergo exchange with primary amines. Thus, treatment of (TTP)Ti=N-*t*-Bu with aniline *does not* afford (TTP)Ti=NPh and free *tert*-butylamine. The reverse reaction of (TTP)Ti=NPh with excess *tert*-butylamine also does not proceed to any observable extent. We have previously shown that the oxo analogue, (TTP)Ti=O rapidly undergoes incomplete oxygen atom transfer with (TTP)Ti(II) species to afford the bridging Ti(III)-oxo dimer [(TTP)Ti]₂(μ-O). In contrast, the imido complexes described above do not react with (TTP)Ti(η²-EtC≡C-Ph) to afford the Ti(III) dimer [(TTP)Ti]₂(μ-NPh). This difference may be due to the steric problems presented by the imido substituents.

Discussion

The (TTP)Ti fragment serves as a useful template for the study of a wide range of metal–ligand multiple bonds. The series (TTP)Ti=X (X = O, S, Se, NR) is now firmly established.¹² In the future, we hope to extend this interesting class of complexes to include other metal–ligand multiply bonded species such as alkylidenes and phosphinidines. In order to design rational syntheses of these complexes, we have attempted to elucidate the mechanism by which the imido ligands are introduced via lithium amides. The formation of imido complexes from **1** and LiNHR must involve α-hydrogen abstraction. Two possible mechanisms are shown in Scheme 1. A concerted intramolecular elimination from the bis(amido) complex is unlikely given the known trans disposition of the amido ligands in (TTP)Ti(NPh)₂ (**5**). A concerted bimolecular pathway in which 2 equiv of H₂NR are simultaneously eliminated from 2 mol of (TTP)Ti(NHR)₂ is also implausible due to the steric nature of the porphyrin ligands. Intermolecular deprotonation of an imido ligand by a second equivalent of LiNHR is a reasonable alternative. Moreover, the strong π-donor character of the amide ligand may facilitate the dissociation of the trans chloride and/or increase the acidity of the α-proton (Scheme 2). This hypothesis is supported by reaction 8 in which only (TTP)Ti=N-*t*-Bu was formed and no

Scheme 3



monoamido complex, (TTP)Ti(NH-*t*-Bu)Cl, was observed on treating **1** with 1 equiv of LiNH-*t*-Bu. Additionally, since other amide reagents (e.g., LiNEt₂) lead only to reduction of Ti(IV) to Ti(III), deprotonation of a primary amide ligand appears to compete effectively with reduction processes. Moreover, our inability to isolate or observe a monoamido complex is consistent with the high acidity of the N–H proton of the complexed amido ligand.

The strong π-donor ability of the amido ligand also provides a rationale for reactions 5 and 8. In the ligand disproportionation (eq 5), the amido ligand prefers to be trans to a weaker chloro ligand than trans to a second strong π-donor amido ligand. Correspondingly, treatment of (TTP)Ti(NPh₂)Cl with LiNH-*t*-Bu (eq 9) is likely to produce transiently the mixed amido complex (TTP)Ti(NPh₂)(NH-*t*-Bu). Competing π-donation serves to labilize both ligands. The loss of the *t*-Bu amide is nonproductive. However, dissociation of NPh₂ produces [(TTP)Ti(NH-*t*-Bu)]⁺ having an acidic α-hydrogen which is rapidly deprotonated to produce (TTP)Ti=N-*t*-Bu.

To the best of our knowledge, the production of imido complexes from Ti(III) sources (reactions 11 and 12) is unprecedented. There are several scenarios one could envision to account for these reactions. It is important to note that (TTP)TiCl does not react with either diphenylacetylene or pyridine to produce (TTP)TiCl₂ and (TTP)Ti(η²-Ph–C≡C–Ph) or (TTP)Ti(py)₂. Thus, (TTP)TiCl does not readily disproportionate. If the reaction of (TTP)TiCl with LiNH-*t*-Bu affords initially (TTP)Ti(NH-*t*-Bu), this species could undergo electron transfer (either in an inner- or outer-sphere sense) with a second Ti(III) species to afford either (TTP)Ti(NH-*t*-Bu)X (X = NH-*t*-Bu or Cl) or [(TTP)Ti(NH-*t*-Bu)]⁺ along with a Ti(II) complex (Scheme 3). The former complex could be deprotonated by an additional equivalent of lithium amide to afford the imido complex while the latter complex is readily trapped by pyridine or diphenylacetylene. However, it is not clear why (TTP)Ti-NH-*t*-Bu would be more prone to disproportionation than (TTP)TiCl. However, on the basis of the observations above, it appears that α-hydrogen abstraction occurs much more rapidly than reduction for Ti-porphyrin complexes. Thus, we propose that any (TTP)Ti(NH-*t*-Bu) formed in the reaction is rapidly deprotonated to afford the transient Ti(III)–imido complex anion [(TTP)Ti=N-*t*-Bu][−]. Due to its anionic charge, this Ti(III)–imido complex presumably is more capable of reducing (TTP)TiCl to Ti(II), which is subsequently trapped by either pyridine or diphenylacetylene.

Conclusions

In this work we have demonstrated that (TTP)TiCl₂, which is readily prepared from the reaction of TiCl₄(THF)₂ with Li₂(THF)₂TTP, serves as a useful precursor for the synthesis of a variety of Ti-porphyrin complexes possessing hard π-donor ligands. Prior to this work, the only reported complexes of this

class of compounds are (TPP)Ti(OMe)¹⁶ and the η^2 -catecholate (TTP)Ti(O₂C₆H₄).¹⁷ We have shown that the Ti(IV)–bis(alkoxides) can be readily produced. Perhaps surprisingly, given the immense number of Ti–amido complexes known,¹⁸ we have found that the only isolable bis(amido)–porphyrin complex is

- (16) Boreham, C. J.; Buisson, G.; Duee, E.; Jordanov, J.; Latour, J.-M.; Marchon, J.-C. *Inorg. Chim. Acta* **1983**, 70, 77–82.
- (17) Marchon, J.-C.; Latour, J.-M.; Grand, A.; Belakhovsky, M.; Loos, M.; Goulon, J. *Inorg. Chem.* **1990**, 29, 57–67.
- (18) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides: Synthesis, Structures, and Physical and Chemical Properties*; John Wiley and Sons: New York, 1980; Chapter 8, pp 472–477.

(TTP)Ti(NPh₂)₂. The imido complexes, given the reactivity displayed by the oxo analogue (*vide supra*), are perhaps of the greatest interest. Of particular interest, is the fact that (TTP)–Ti=NR complexes may be isolated starting from Ti–porphyrin complexes in various oxidation states.

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